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Corrected spherical model for vacancies in simple metals

F. Perrot

Commissariat à l'Energie Atomique, Centre d'Etudes de Limeil, Boîte Postale 27, 94190 Villeneuve-Saint-Georges, France

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The energy required to create a vacancy in a simple metal is written, apart from the lattice relaxation energy, as the sum of two terms. One is the binding energy E_b of an atom in the perfect solid; the other represents the difference between the energies of the defected and perfect crystals in the same volume. This second term is estimated, using the spherical-solid model, as the difference of two self-consistent calculations of total energies within the local-density formalism. The ions surrounding the defect are simulated by pseudopotentials. The spherical approximation of the perfect lattice is obtained by adding the "exact" ionic potential at the center of the defected lattice. This exact potential results from a self-consistent augmented-plane-wave calculation of the perfect solid, which also gives the binding energy E_b. The magnitude of the nonspherical ionic potential contribution to the vacancy energy is then investigated, using different linear-response functions for the perfect and defected systems. Satisfying agreement with experiment is obtained for the alkali metals Li, Na, and K, but the model fails for high-electron-density metals as Al.

I. INTRODUCTION

Large attention has been paid recently to the energetics of defects in metals. The standard theory of pseudopotentials, with expansion of the binding energy up to second or third order in electron-ion interaction, has been applied to vacancy-formation-energy calculations in simple metals.[1-6] The weakness of this approach lies in the use of the free-electron linear-response function for both of the perfect and defected lattices. In fact, the depletion of the density around the vacancy induces in that region a decrease of the electron polarizability which should be taken into account. A second class of schemes for vacancies includes the jellium model and all its improvements dealing with the perturbative treatment of the ionic potential, written as a superposition of pseudopotentials.[7-11] Neither zero-order nor first-order jellium results, as obtained by Manninen *et al.*, give quantitative agreement with experiment.[8] Including the second-order corrections, as done by Evans and Finnis, does not lead to satisfying values.[10,11] But they were calculated with the inadequate free-electron-gas susceptibility for the defected lattice, so that they may be suspected.

In a previous paper,[12] we have proposed to adapt the spherical-solid model (SSM) of Almbladh and von Barth[13] to the self-consistent density calculation for vacancies in simple metals. In that model, potential and electron density are spherically averaged around the defect; the total energy is calculated using the density-functional formalism of Hohenberg and Kohn.[14,15] The vacancy-formation-energy is written

$$E_f = E_{\Delta\mathrm{SCF}} + E_b\,, \qquad (1)$$

$$E_{\Delta\mathrm{SCF}} = E_d(N-1,\Omega) - E_p(N,\Omega)\,.$$

$E_{\Delta\mathrm{SCF}}$ is the energy required to remove one atom from the solid at constant volume Ω. $E_{\Delta\mathrm{SCF}}$ is thus the difference between the energies of the defected lattice (without atom at origin, $N-1$ atoms in the solid) and the perfect lattice (one atom at origin, N atoms in the solid) in the volume Ω. The binding energy E_b of an atom in the perfect lattice must be added to $E_{\Delta\mathrm{SCF}}$ in order to obtain E_f: E_b is the energy needed to add the removed atom in the bulk of the solid. The approximation proposed in Ref. 12 was to estimate $E_{\Delta\mathrm{SCF}}$ as the difference of two SSM calculations, one for the defected lattice and the other for the perfect lattice. In both cases, an empty-core Ashcroft model potential represented the bare ion. The binding energy E_b was calculated up to third order in electron–ion interaction. The results improved significantly the semilinear-screening values of Evans and Finnis,[11] but good agreement with experiment was not obtained.

In this paper we report several refinements of the calculations based on the SSM applied to the description of vacancies, leading to a more accurate treatment of the problem. In Sec. II, we give a detailed description of the model, where the true ion, instead of a pseudoion, is placed at the center of the perfect lattice. We comment the corresponding expression of $E_{\Delta\mathrm{SCF}}$ and the calculation of E_b. Section III is concerned with the specification of the model potential for the noncentral ions. The effect of the nonspherical component of the ionic potential is investigated in Sec. IV where an approximate linear-response function for the perturbed lattice is derived, using the Thomas-Fermi semiclassical theory. Numerical results for the alkali metals Li, Na, and K, and for aluminum are reported and discussed in Sec. V.

II. SPHERICAL SOLID MODEL FOR A VACANCY

The accurate calculation of defects in solids is very difficult because lattice periodicity is broken. Simplified models must be worked out in order to avoid considerable computational effort. The SSM, applied by Almbladh and von Barth[13] to the calculation of highly localized excitations in metals, is very appealing in that sense. SSM is expected to be relevant when the effect of the impurity vanishes within a distance less than the Wigner-Seitz (WS) radius. This is not the case for vacancies in solids which extend as far as two or three WS radii (the Friedel oscillations extend even further). Nevertheless, we assume that there is an important cancellation of the errors when the difference in energy $E_{\Delta S\,CF}$ of the two spherical systems is calculated. The reason is that the nonspherical component of the potential is negligible in the region where the displaced density is very large (inside the WS sphere); and conversely, the screening of the defect is important where the nonspherical potential is strong. We shall go further into detail on this point and give an estimate of the nonspherical contribution in Sec. IV.

The noncentral ions in the two systems of interest (defected and perfect solids) are described by means of a local pseudopotential $w(\vec{r})$. The total ionic potential for the defected case is $\sum_i' w(\vec{r}-\vec{R}_i)$. The spherical average of this potential is easily expressed using the Fourier transform of the lattice sum

$$\left\langle \sum_i{}' w(\vec{r}-\vec{R}_i) \right\rangle = U(r) - w(r) + U_0 - \frac{1}{r} * n_0, \tag{2}$$

$$U(r) = \frac{1}{\Omega_0} \sum_{\vec{K}}{}' w(\vec{K}) \frac{\sin Kr}{Kr} . \tag{3}$$

The angular brackets on the left-hand side of Eq. (2) indicate spherical averaging around the center $\vec{r}=0$. The asterisk has been used for the convolution product

$$f * g = \int f(\vec{r}-\vec{r}\,')\, g(\vec{r}\,')\, d\vec{r}\,' .$$

The volume of the WS sphere is Ω_0 and $\vec{K}$ is a reciprocal-lattice vector; $w(\vec{q})$ is the standard Fourier transform

$$w(\vec{q}) = \int w(\vec{r}) e^{i\vec{q}\cdot\vec{r}} d\vec{r} .$$

U_0 is a constant defined by

$$U_0 = \frac{1}{\Omega_0} \lim_{q\to 0} \left(w(\vec{q}) + \frac{4\pi Z}{q^2} \right), \tag{4}$$

where Z is the valence of the metal in which the mean electron density is $n_0 = Z/\Omega_0$. In the following text, we shall label the quantities relative to the defected lattice by the index d and those relative to the perfect lattice by the index p.

The ionic potential of the perfect lattice is obtained by adding to Eq. (2) the potential of the ion located at $\vec{r}=0$. As an accurate description of the central WS sphere is essential, we chose to use at $\vec{r}=0$ the true potential of the ion, resulting from a self-consistent augmented-plane-waves (APW) calculation of the perfect solid, instead of the pseudopotential $w(\vec{r})$. This choice has also the advantage to remove uncertainties in the calculation of the binding energy: E_b is obtained from the APW calculation of the potential, correct to all orders in electron-ion interaction, instead of order two or three when a perturbative expansion of E_b is used. The Hartree potential of the ion is

$$v(r) = -Z_i/r + \langle (1/r) * n_c \rangle ,$$

where Z_i is the atomic number of the metal and $n_c(r)$ the self-consistent APW density of the core electrons in the ion.

The valence-valence exchange and correlation potential $\mu_{xc}(n)$ (n is the valence density) is given, according to the density-functional formalism,[14] by the relation

$$\mu_{xc} = \frac{d}{dn}(n\epsilon_{xc}) . \tag{5}$$

ϵ_{xc} is the exchange and correlation energy functional. We have used the Wigner interpolation formula [with $r_s(n)$ defined by $\frac{4}{3}\pi r_s^3(n) = n^{-1}$]

$$\epsilon_{xc}(n) = \epsilon_{KS}(n) - 0.44/[r_s(n) + 7.80] , \tag{6}$$

where ϵ_{KS} is the Kohn–Sham functional[16]

$$\epsilon_{KS}(n) = -\tfrac{3}{4}[(3/\pi)n]^{1/3} . \tag{7}$$

In our model for the perfect lattice, there exists also an exchange and correlation interaction between the core electrons of the central ion and the valence electrons. This contribution is written $\mu_{KS}(n_c+n_p) - \mu_{KS}(n_p)$.

Finally, apart from a constant term $U_0 + \mu_{xc}(n_0)$, the total potentials are, in the defected and perfect lattices, respectively,

$$V_d(r) = U(r) - w(r) + (1/r)*(n_d - n_0) + \mu_{xc}(n_d) - \mu_{xc}(n_0) , \tag{8}$$

$$V_p(r) = U(r) - w(r) + v(r) + (1/r)*(n_p - n_0) + \mu_{KS}(n_c+n_p) - \mu_{KS}(n_p) + \mu_{xc}(n_p) - \mu_{xc}(n_0) . \tag{9}$$

Each of these potentials decreases to zero faster than r^{-1} for large r, so that each problem may be handled as an impurity problem. The technique of solving self-consistently the corresponding Schrödinger equations is now well known[8,13,17] and will not be detailed here. When the self-consistent wave functions and phase shifts $\delta_l(k)$ for all the angular momenta l and wave vectors $\vec{k}$ of the occupied states have been calculated in the perfect and defected cases, respectively, the computation of $E_{\Delta\mathrm{SCF}}$ can be achieved, according to the following formulas

$$E_{\Delta\mathrm{SCF}} = -2\epsilon_M - ZU_0 - Z\mu_{xc}(n_0) - \frac{Z}{2}k_F^2 + \frac{1}{2}\int_\Omega \frac{Z}{r}(n_d - n_0)\,d\vec{r} + G(n_d) - G(n_p) + E_{xc}(n_d) - E_{xc}(n_p) - M_{xc}(n_d) + M_{xc}(n_p), \quad (10)$$

$$G(n) = -\frac{2}{\pi}\int_0^{k_F} k\,dk \sum_l (2l+1)\delta_l(k) - \frac{1}{2}\int_\Omega (n+n_0)\left(\frac{1}{r} * (n-n_0) + \alpha\frac{Z}{r}\right)d\vec{r}, \quad (11)$$

$$E_{xc}(n) = \int_\Omega [n\epsilon_{xc}(n) - n_0\epsilon_{xc}(n_0) + \beta n_t \epsilon_{\mathrm{KS}}(n_t) - \beta n \epsilon_{\mathrm{KS}}(n)]\,d\vec{r}, \quad (12)$$

$$M_{xc}(n) = \int_\Omega [n\mu_{xc}(n) - n_0\mu_{xc}(n_0) + \beta n \mu_{\mathrm{KS}}(n_t) - \beta n \mu_{\mathrm{KS}}(n)]\,d\vec{r}. \quad (13)$$

ϵ_M is the Madelung energy of the perfect crystal; k_F is the Fermi momentum. The parameter α has the value $\alpha_p = 0$ in the perfect solid and $\alpha_d = 1$ in the defected solid; the parameter β is $1-\alpha$. The total (core plus valence density in the perfect spherical solid is $n_t = n_c + n_p$.

As indicated above, the density $n_c(r)$ of the core electrons in the ion and the binding energy E_b of an atom in the perfect solid were calculated by the self-consistent APW method, in the muffin-tin form of density and potential. In this calculation, the exchange and correlation energy was treated in an exactly similar way, using the expression

$$\int_\Omega [n_v\epsilon_{xc}(n_v) + (n_c + n_v)\epsilon_{\mathrm{KS}}(n_c + n_v) - n_v\epsilon_{\mathrm{KS}}(n_v)]\,d\vec{r}$$

for the total energy. The APW valence density is $n_v(r)$. The contribution of the isolated ion

$$\int_{\Omega_0} n_c \epsilon_{\mathrm{KS}}(n_c)\,d\vec{r}$$

must be subtracted from the total energy to obtain the exchange and correlation contribution to the binding energy.

III. SPECIFICATION OF THE PSEUDOPOTENTIAL FOR SURROUNDING IONS

A local pseudopotential was used in Ref. 12 for the central ion in the perfect lattice. But it is a well-known result that local pseudopotentials are inadequate to describe the band structure of lithium. The question of using a nonlocal pseudopotential thus rises naturally. According to the philosophy of SSM, which is that the impurity is not very sensitive to the details of the potential due to neighboring atoms, it was assumed that only the central ion for the perfect-lattice calculation should be treated with a high degree of accuracy. Consequently, we thought that the simulation of surrounding sites by a local potential was coherent with the model. The great advantage of locality is to allow the easy computation of the superposed potential $U(r)$ [Eq. (4)]. For the ion at $\vec{r} = 0$, the use of the true potential $v(r)$ was obviously the best solution.

The simplest choice for a local potential is the empty core potential; its smoothed form, as suggested by Cohen and Heine,[18]

$$w(q) = -(4\pi Z/q^2)\cos qR_c\, e^{-(q/q_0)^2} \quad (14)$$

has considerable practical interest for the computation of $U(r)$, since the good convergence of Eq. (14) avoids the use of the Ewald-Fuchs technique of double summation in real and reciprocal spaces. We have fixed the value of q_0 to $5.5k_F$ for all the metals. It will be shown in Sec. V that the results are not sensitive to this particular choice. The only parameter in Eq. (14) to be carefully adjusted is R_c. The criterion is that $w(q)$ reproduces the APW binding energy E_b of an atom in the perfect solid. The binding energy is very easily calculated up to second order in $w(q)$; its expression $E_{b2}(w)$ can be found in Ref. 19. Exchange and correlation as defined in Eq. (6) has been used both in the zero-order term and in the function $\mathcal{G}(q)$ appearing in the interacting response function. The radius R_c is determined by the relation

$$E_{b2}(w) + \Delta = E_b, \quad (15)$$

where E_b is the APW binding energy and Δ a corrective term taking into account the contribution of all the orders $w^n(q)(n \geq 3)$ not included in $E_{b2}(w)$. Δ has been computed once in the case of the Ashcroft model potential w_A, with the parameter given by Shyu and Gaspari,[20] as the difference between the binding energy resulting from an APW calculation with the frozen ionic potential w_A and $E_{b2}(w_A)$. Then, for a given metal, Δ has been considered as a constant when applying Eq. (15).

In order to test the influence of the pseudopotential on our calculations, we have also defined a two-parameters model potential, corresponding to a smoothed well

$$w(q) = -\frac{4\pi Z}{q^2}\left(D\frac{\sin qR_c}{qR_c} + (1-D)\cos qR_c\right)e^{-(q/q_0)^2}. \quad (16)$$

The following condition was added to Eq. (15): it was required to fit the APW valence density $n_v(r)$ as best as possible with the muffin-tin component $n_{l\,\mathrm{mt}}$ of the density n_l induced by w in the perfect solid and calculated by linear-response theory. We defined the quantity

$$s^2(w)=\frac{1}{\Omega_0}\int_{\Omega_0}(n_v-n_{l\,\mathrm{mt}})^2\,d\vec{r} \tag{17}$$

and determined the parameters D and R_c by simultaneously solving Eq. (15) and minimizing Eq. (17). In lithium and sodium, this procedure gives a value of D nearly equal to zero. In potassium and aluminium, the difference between the two potentials (14) and (16) is more important, as the numerical results will show in Sec. V.

IV. NONSPHERICAL CONTRIBUTION TO THE VACANCY FORMATION ENERGY

A semiquantitative study of the contribution of the ionic potential nonspherical component was undertaken with the only object to check its smallness. But we had to conclude from our calculations that this contribution is not negligible and depends rather strongly on the parameters of the model potential. It must be taken into account for a correct numerical estimate of E_f in the alkali metals. In aluminium, it is even much larger than E_f as defined by Eq. (1). We shall now use the notations

$$E_f^v=E_f^s+E_f^{\mathrm{ns}}\,, \tag{18}$$

$$E_f^s=E_{\Delta\mathrm{SCF}}+E_b\,. \tag{19}$$

E_f^v is the energy needed to create a vacancy without any lattice relaxation. E_f^v is the sum of two terms; the first one is E_f^s which is calculated in the SSM model, the second, E_f^{ns} is due to the nonspherical ionic potential. The full vacancy formation energy to compare with experiment also includes a relaxation energy E_R,[1]

$$E_f=E_f^v+E_R\,. \tag{20}$$

The term E_f^{ns} will be estimated as a second-order perturbation, the perturbative potential being

$$\delta V_i(\vec{r})=\frac{1}{\Omega_0}\sum_{\vec{K}}{}'\,w(K)\left(e^{i\vec{K}\cdot\vec{r}}-\frac{\sin Kr}{Kr}\right). \tag{21}$$

As a consequence of its spherical symmetry, the potential centered at $\vec{r}=0$ does not appear in the perturbation (21), which is the same for the perfect and defected lattices. The first-order perturbation energy vanishes since both $n_d(r)$ and $n_p(r)$, the SSM electron densities, are spherical. E_f^{ns} reduces to the second-order term

$$E_f^{\mathrm{ns}}=\frac{1}{2}\int_\Omega(\delta n_d-\delta n_p)\,\delta V_i\,d\vec{r}\,. \tag{22}$$

δn_d and δn_p are the densities induced by $\delta V_i(\vec{r})$ in the defected and perfect lattice, respectively. They must be calculated with the appropriate linear-response functions of the two systems, which are different. The modification of the wave functions from a system to the other affects the matrix elements in the expression of the polarizability. Furthermore, terms $O(N^{-1})$ (N is the number of atoms in the solid) in the response function of the defected lattice contribute to the vacancy energy, so that the variation of the Fermi momentum and the one-electron levels, proportional to N^{-1}, should be taken into account. Such a task clearly requires a too important computational effort. We restricted ourself to a much less sophisticated treatment, using the linearized Thomas-Fermi (TF) theory. The change in density δn is related to the change in potentials by

$$\pi^2\delta n=-[2(E_F-V)]^{1/2}(\delta V_i+\delta V_e)\,. \tag{23}$$

V is the total potential (ion plus electrons) in the ground state and its change is $\delta V_i+\delta V_e$. The Fermi energy is E_F, identical in the perfect and defected systems since the density n_0 ($\propto E_F^{3/2}$) at large distances is identical. The electronic potential δV_e is related to δn by the Poisson equation so that Eq. (23) becomes

$$(\Delta-\lambda^2)\delta V_e=\lambda^2\delta V_i\,, \tag{24}$$

$$\lambda^2(r)=(4/\pi)\{2[E_F-V(r)]\}^{1/2}=4[(3/\pi)n_d]^{1/3}\,. \tag{25}$$

Equation (24) can be solved in δV_e if the Green's function $G(\vec{r},\vec{r}\,')$ satisfying the equation

$$[\Delta-\lambda^2(r)]G(\vec{r},\vec{r}\,')=-4\pi\delta(\vec{r}-\vec{r}\,') \tag{26}$$

is known. In the perfect crystal, λ^2 is a constant $[\lambda_p^2=4(2E_F)^{1/2}/\pi]$ and $G_p(\vec{r},\vec{r}\,')$ is

$$G_p(\vec{r},\vec{r}\,')=e^{-\lambda_p|\vec{r}-\vec{r}\,'|}/|\vec{r}-\vec{r}\,'|\,. \tag{27}$$

The solution of Eq. (26) for the defected case is obtained as an expansion in G_p,

$$G_d(1,2)=G_p(1,2)+\delta G_1(1,2)+\delta G_2(1,2)+\cdots\,,$$
$$(-4\pi)\delta G_1(1,2)=\int G_p(1,3)f(3)G_p(3,2)\,d(3)\,, \tag{28}$$

$$(-4\pi)\delta G_2(1,2)=\int G_p(1,3)f(3)\delta G_1(3,2)\,d(3)\,,$$
$$f(r)=\lambda_d^2(r)-\lambda_p^2\,. \tag{29}$$

The obvious notation of Hedin[21] has been used in the expansion of δG. The solution of Eq. (24) is

$$-4\pi\delta V_e(1)=\int G(1,2)\lambda^2(2)\delta V_i(2)\,d(2)$$

and

$$(4\pi)^2\delta n(1)=\lambda^2(1)\int G(1,2)\lambda^2(2)\delta V_i(2)d(2)$$
$$-4\pi\lambda^2(1)\delta V_i(1)\,. \tag{30}$$

We are now in position to write the nonspherical contribution E_f^{ns}, up to first order in f,

$$E_f^{\text{ns}}=(4\pi)^{-2}\lambda_p^2\int\int\delta V_i(1)$$
$$\times[f(1)G_p(1,2)+\tfrac{1}{2}\lambda_p^2\delta G_1(1,2)]$$
$$\times\delta V_i(2)d(1,2)$$
$$-2\pi\int f(1)\delta V_i^2(1)d(1)\,. \tag{31}$$

The transformation of Eq. (31) in reciprocal space is straightforward and the following very compact result is derived:

$$E_f^{\text{ns}}=-\tfrac{1}{4}(2\pi)^{-7}\int\int\delta\overline{V}_i(\vec{q})f(|\vec{q}-\vec{q}'|)$$
$$\times\delta\overline{V}_i(\vec{q}')\,d\vec{q}\,d\vec{q}'\,, \tag{32}$$

where $\delta\overline{V}_i(\vec{q})$ is the Fourier component of the screened potential, i.e., $\delta V_i(\vec{q})$ divided by the TF dielectric constant

$$\delta\overline{V}(\vec{q})=[q^2/(q^2+\lambda_p^2)]\,\delta V(\vec{q})\,. \tag{33}$$

The Fourier transform of the perturbation $\delta V_i(\vec{r})$ defined by Eq. (21) is

$$\delta V_i(\vec{q})=\frac{(2\pi)^3}{\Omega_0}\sum_{\vec{K}}{}'\,w(K)\left(\delta(\vec{K}-\vec{q})-\frac{1}{4\pi K^2}\,\delta(K-q)\right). \tag{34}$$

$\delta(K-q)$ is a one-dimensional δ distribution which is nonzero when the vectors $\vec{K}$ and $\vec{q}$ have the same length. Combining Eqs. (32) and (34) leads to the final result

$$E_f^{\text{ns}}=-\frac{1}{8\pi\Omega_0^2}\sum_{\vec{K}}{}'\sum_{\vec{K}'}{}'\,\overline{w}(K)\overline{w}(K')$$
$$\times\left(f(|\vec{K}-\vec{K}'|)\right.$$
$$\left.-\frac{1}{2KK'}\int_{|K-K'|}^{K+K'}q\,dq\,f(q)\right). \tag{35}$$

Plots of the TF density for defects are reported in the paper by Manninen *et al.*[8] We have used their curves to generate the analytical forms

$$\lambda_d^2(r)=\lambda_p^2[1-A\tfrac{1}{3}(\beta/\pi)^{3/2}e^{-\beta r^2}]\,, \tag{36}$$

requiring the most accurate fitting in the region $r\sim R_{\text{WS}}$. Such a representation is very convenient for the calculation of Eq. (35) since it gives

$$f(q)=-A(\tfrac{1}{3}\Omega_0)\lambda_p^2e^{-q^2/4\beta}\,. \tag{37}$$

TABLE I. Wigner-Seitz radius R_{WS} and average electron density n_0 (atomic units) for the present calculations. The binding energy E_b used in the vacancy energy calculations is E_b(APW); E_b(ANA) results from the auxiliary-neutral-atom method[17] and is given for comparison. The experimental values are shown in the last column. All are in rydbergs.

	R_{WS}	n_0	E_b(APW)	E_b(ANA)	E_b(exp)
Li	3.25	0.006 95	−0.5393	−0.5394	−0.5202
Na	3.93	0.003 93	−0.4907	−0.4882	−0.4616
K	4.86	0.002 08	−0.4111	−0.4090	−0.3890
Al	2.985	0.026 93	−4.2346		−4.168

In this section, we have established an expression of the nonspherical contribution to the vacancy formation energy. The approximations involved in this formula are: (i) use of the TF linear-response function; (ii) calculation to first order in the difference $f=\lambda_d^2-\lambda_p^2$; (iii) analytical fitting of the TF density. As shown by Eq. (37), E_f^{ns} is very sensitive to the exponent β, which depends on the relative importance attributed to the long ranges $r>R_{\text{WS}}$ in the fitting of $\lambda_d^2(r)$. A large uncertainty is inherent to this description which must be considered as a phenomenological model only.

V. NUMERICAL RESULTS AND DISCUSSION

In this section are reported the numerical results of the present work. Our model has been applied to the alkali metals Li, Na, and K and to aluminum.

A. Binding energy

As explained in Sec. II, the binding energy E_b of an atom in the perfect solid has been calculated for each one of the metals using the standard APW method. For the bcc lattice, Brillouin-zone integration has been done on a 1024 points mesh, and for the fcc lattice, on a 256 points mesh. The numerical errors are estimated to be less than 0.001 Ry on E_b. The values of the binding energy, together with some quantities of interest, as the WS

TABLE II. Parameters defining the first pseudopotential (PP1), or smoothed empty core (Eq. 14). Δ is an approximate correction added to the second-order binding energy to get the exact binding energy.

	Z	R_c	$q_0=5.5k_F$	Δ (Ry)
Li	1	1.29	3.2478	0.0076
Na	1	1.53	2.6858	0.0046
K	1	2.10	2.1720	0.0044
Al	3	1.09	5.1000	0.0765

TABLE III. Minimization of the mean error $s(w)$ between APW and linear-response theory (LRT) valence densities for lithium. The pseudopotential used in LRT is the smoothed well pseudopotential, with core radius R_c and depth $-ZD/R_c$, which fits the binding energy. The value of q_0 in the damping function is $q_0=5.5k_F$.

R_c	D	$s(w)$
1.00	−1.30	2.231×10^{-3}
1.20	−0.257	2.091×10^{-3}
1.30	0.033	2.081×10^{-3}
1.40	0.252	2.087×10^{-3}
1.60	0.555	2.119×10^{-3}

radius and the mean electron density n_0, are given in Table I. The theoretical values of E_b obtained by Dagens[17] in the auxiliary neutral-atom model (with Nozières-Pines instead of Wigner correlation) and the experimental values of E_b are shown for comparison.

B. Pseudopotentials

Two choices have been done for the pseudopotentials simulating the ions not located at the center of the spherical model. In the first one, the binding energy calculated with the pseudoion is adjusted on the APW binding energy, according to Eq. (15). The values of Δ used in Eq. (15) and the core radius R_c determined in such a way are shown in Table II. This pseudopotential will be referred to as PP1 in the following discussion. We checked with PP1 the small influence of the damping factor q_0: in Na, the change in $E_{\Delta\mathrm{SCF}}$ is 6×10^{-3} eV when q_0 varies from 5 to $6k_F$.

TABLE IV. Parameters for the smoothed well pseudopotentials (PP2), with core radius R_c and depth $-ZD/R_c$ ($q_0=5.5k_F$, see Table II).

	R_c	D
Li	1.26	−0.070
	1.32	0.081
Na	1.50	−0.075
	1.56	0.063
K	2.30	0.300
Al	1.23	0.398

For the second (smoothed-well) pseudopotential PP2, the variations of $s(w)$ as a function of R_c at constant binding energy have been studied. In lithium and sodium, the corresponding curves are very flat near their minimum, approximately obtained for the parameter R_c of PP1. As an example, the variations of $s(w)$ in Li are shown in Table III. Nevertheless, in order to appreciate the effect of varying the pseudopotential, we have defined in Li and Na two pseudopotentials PP2 corresponding to arbitrary changes $\Delta R_c=\pm0.3$ with respect to PP1. In K, the minimization procedure gives a core radius $R_c=2.30$ for PP2, to compare with $R_c=2.10$ for PP1. In aluminum, a rather accurate minimum is obtained for $R_c=1.23$. The results for the PP2 potentials are summarized in Table IV.

C. SSM calculations

With these numerical values of the pseudopotential parameters, the SSM calculation of $E_{\Delta\mathrm{SCF}}$ has been performed. The potential $U(r)$ [Eq. (3)] has

TABLE V. Vacancy-formation energies in Li, Na, K, and Al. $E_{\Delta\mathrm{SCF}}$ is calculated in the spherical solid model for various pseudopotentials simulating the surrounding ions. E_f^s is obtained by adding the binding energy to $E_{\Delta\mathrm{SCF}}$. The sum of the spherical and nonspherical terms, E_f^s and E_f^{ns}, respectively, gives the vacancy energy at constant volume E_f^v. Adding the relaxation energy E_R gives the total vacancy-formation energy to compare with experiment.

	Pseudopotential	$E_{\Delta\mathrm{SCF}}$ (Ry)	E_f^s (Ry)	E_f^s (eV)	E_f^{ns} (eV)	E_f^v (eV)	E_R (eV)	E_f (eV)	Expt.
Li	PP1 $R_c=1.29$	0.5641	0.0248	0.338	0.064	0.402	−0.09	0.31	0.34 ± 0.04 [a]
	PP2 $R_c=1.26$	0.5643	0.0250	0.340	0.073	0.413	−0.09	0.32	
	PP2 $R_c=1.32$	0.5639	0.0246	0.335	0.057	0.392	−0.09	0.30	
Na	PP1 $R_c=1.53$	0.5229	0.0322	0.439	0.052	0.491	−0.11	0.38	0.42 ± 0.03 [b]
	PP2 $R_c=1.50$	0.5231	0.0324	0.441	0.058	0.499	−0.11	0.39	
	PP2 $R_c=1.56$	0.5227	0.0320	0.436	0.040	0.476	−0.11	0.37	
K	PP1 $R_c=2.10$	0.4445	0.0334	0.455	0.074	0.529	−0.12	0.41	0.39 [c]
	PP2 $R_c=2.30$	0.4434	0.0323	0.439	0.037	0.476	−0.12	0.36	
Al	PP1 $R_c=1.09$	4.2470	0.0124	0.169	1.180	1.349	−0.04	1.31	0.66 ± 0.04 [d]
	PP2 $R_c=1.23$	4.2328	−0.0018	−0.024	0.517	0.493	−0.04	0.45	0.69 ± 0.03 [e]

[a] Reference 24.
[b] Reference 25.
[c] Reference 26.
[d] Reference 27.
[e] Reference 28.

TABLE VI. Parameters, as estimated from the calculations by Manninen *et al.*,[8] for Thomas-Fermi linear-response function of the defected lattice.

	β	A
Li	0.100	1.411
Na	0.074	1.371
K	0.047	1.645
Al	0.128	1.505

been obtained by a straightforward summation in reciprocal space, for $\vec{K}$ vectors up to a length of $12 \times 2\pi/a$ (a is the lattice parameter). The spherical solid was confined in a box of radius $R_s = 8R_{\rm WS}$. The mesh of points for numerical integration was divided into an exponential region (step of approximately 0.03) for small r and an arithmetic region (step of approximately $\pi/30k_F$) for large r. In order to obtain a good convergence in the angular momentum expansion ($l \leq l_m$), $U(r)$ was truncated at a radius R_M and replaced by 0 for r larger than R_M, where its effect was then treated as a perturbation. In lithium for instance, the difference between the values of $E_{\Delta \rm SCF}$ for a calculation with $l_m = 7$ and $R_M = 6.92$ a.u., and a calculation with $l_m = 10$ and $R_M = 10.22$ a.u. $[l_m(l_m+1)/R_M^2 = \text{const}]$ is 2.10^{-5} Ry, showing that the perturbative treatment of $U(r)$ in the region $r > R_M$ is perfectly accurate. A step $\Delta k = 0.025$ has been used for integration in k space. For a description of the numerical technique applied to the iterative process, the reader will refer to the paper by Manninen *et al.*[8]

The improvement due to the use of the exact ion at the center of the perfect lattice has been tested. In the case of lithium, where the effect is large, the substitution of the pseudopotential PP1 to the exact ion at the center causes a 0.003 Ry decrease in $E_{\Delta \rm SCF}$ (12% of E_f). In Al, it causes an increase in $E_{\Delta \rm SCF}$ as large as 0.047 Ry (95% of E_f).

In Table V are shown the numerical values of $E_f^{\rm s}$ [Eq. (18)] for the various pseudopotentials PP1 and PP2. Although these numbers do not represent the measured vacancy formation energy, we notice that their magnitude is comparable with experimental data in the alkali metals. On the other hand, $E_f^{\rm s}$ is much smaller than experiment for aluminum, and even negative with potential PP2. The nonspherical contribution $E_f^{\rm ns}$ is thus expected to be very large in Al.

D. Nonspherical contribution

The simple model described in Sec. IV [Eq. (35)] has been applied to the calculation of the nonspherical contributions to the vacancy energy. In Table VI we show the values of the parameters β and A in the analytical form of $f(q)$ [Eq. (37)]. The results for $E_f^{\rm ns}$ are given in Table V. For the alkali metals, $E_f^{\rm ns}$ typically amounts to 10% or 20% of $E_f^{\rm s}$, with important changes when the radius R_c is varied. Nevertheless, this term remains small enough to justify our approximate treatment. The situation is entirely different in Al, where $E_f^{\rm ns}$ is much larger than $E_f^{\rm s}$. This fact is not surprising indeed, since δV_i is proportional to Z, f to $Z^{1/3}$, so that $E_f^{\rm ns}$ is proportional to $Z^{7/3}$; the mean value being about 0.06 eV in the alkalis, a contribution of the order of 0.80 eV may be expected in Al. We find 1.180 eV for PP1 and 0.517 eV for PP2. We conclude that the treatment of $E_f^{\rm ns}$ as a corrective term is not founded in Al, and that the nonspherical ionic potential should be treated on the same basis as the spherical one. The SSM approach to defects is probably irrelevant for metals with a valence greater than one.

E. Comparison with experiment and conclusion

According to Eq. (20), the relaxation energy E_R must be added to $E_f^{\rm v} = E_f^{\rm s} + E_f^{\rm ns}$ before comparison with experiment. For the alkali metals we have used the values of E_R calculated by Ho[1] in local pseudopotentials, and for Al the value of Finnis and Sachdev.[22] Of course, these numbers do not exactly correspond to our pseudopotentials PP1 and PP2, but they allow an estimate of the total vacancy-formation energy. In the alkali metals, the full E_f are in satisfying agreement with experiment. The spherical model is well suited for vacancies in monovalent metals and accurate vacancy-formation energies will be calculated provided that a more careful linear-response theory will be applied to the nonspherical term. The recent work by Kahn and Rasolt[23] seems to be very promising in that way. For divalent or trivalent metals, the model is hopeless and cluster calculations are likely the relevant approach to the problem.

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[1] P. S. Ho, Phys. Rev. B **3**, 4035 (1971).

[2] R. Chang and L. M. Falicov, J. Phys. Chem. Solids **32**, 465 (1971).

[3] Z. D. Popovic, J. P. Carbotte, and G. R. Piercy, J. Phys. F **4**, 351 (1974).

[4] P. Minchin, A. Meyer, and W. H. Young, J. Phys. F **4**, 2117 (1974).

[5] S. Tanigawa and M. Doyama, Phys. Status Solidi B **73**, 517 (1976).

[6] S. Yoshioki and G. Mori, J. Phys. F **6**, 1743 (1976).

[7] R. Nieminen, M. Manninen, P. Hautojärvi, and J. Arponen, Solid State Commun. **16**, 831 (1975).

[8] M. Manninen, R. Nieminen, P. Hautojärvi, and J. Arponen, Phys. Rev. B **12**, 4012 (1975).

[9] G. G. Robinson and P. F. de Chatel, J. Phys. F **5**, 637 (1975).

[10] M. W. Finnis, J. Phys. F **5**, 2227 (1975).

[11] R. Evans and M. W. Finnis, J. Phys. F **6**, 483 (1976).

[12] F. Perrot, Phys. Status Solidi B **81**, 205 (1977).

[13] C. O. Almbladh and U. von Barth, Phys. Rev. B **13**, 3307 (1976).

[14] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1965).

[15] N. D. Lang and W. Kohn, Phys. Rev. B **1**, 4555 (1970).

[16] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[17] L. Dagens, J. Phys. C **5**, 2333 (1972); J. Phys. (Paris) **34**, 879 (1973).

[18] M. L. Cohen and V. Heine, in *Solid State Physics*, edited by F. Seitz, E. Turnbull, and H. Ehrenreich (Academic, New York, 1970), Vol. 24, p. 111.

[19] W. Harrison, in *Pseudopotentials in the Theory of Metals* (Benjamin, New York, 1966), p. 23.

[20] W. M. Shyu and G. D. Gaspari, Phys. Rev. **170**, 687 (1968).

[21] L. Hedin and S. Lundqvist, in *Solid State Physics*, edited by F. Seitz, E. Turnbull, and H. Ehrenreich (Academic, New York, 1969), Vol 23, p. 1.

[22] M. W. Finnis and M. Sachdev, J. Phys. F **6**, 965 (1976).

[23] L. M. Kahn and M. Rasolt (unpublished).

[24] R. Feder, Phys. Rev. B **2**, 828 (1970).

[25] R. Feder and H. P. Charbnau, Phys. Rev. **149**, 464 (1966).

[26] D. K. C. McDonald, J. Chem. Phys. **21**, 177 (1953).

[27] B. T. A. McKee, W. Triftshauser, and A. T. Stewart, Phys. Lett. **28**, 358 (1972).

[28] P. Tzanetakis, J. Hillairet, and G. Revel, Phys. Status Solidi B **75**, 433 (1976).